Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Catalytic conversion of methanol/ethanol to isobutanol – a highly selective route to an advanced biofuel

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Experimental

General considerations

All procedures were carried out under an inert atmosphere (N_2) using standard Schlenk line techniques or in an inert atmosphere glovebox (Ar). Chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Solvents were purified using an anhydrous Engineering Grubbs-type solvent system except anhydrous ethanol and methanol which were purchased from Sigma-Aldrich and used as received. Complexes **1**,[1] **2**,[2] **3**,[3] **4**[4] and **6**[5] were synthesised by literature methods. NMR spectra were recorded on a Jeol ECS300 or a Varian VNMRS500 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts were referenced relative to the residual solvent resonances in the deuterated solvent. ^{31}P{^{1}H} NMR spectra were referenced relative to 85% H_3PO_4 external standard. Mass spectra (ESI) were recorded on a Bruker Daltonics micrOTOF II. All catalytic samples were analysed by GC-FID, using an Agilent 7820A GC, fitted with a DB-WAX capillary column, 30 m x 0.32 mm, I.D. 0.25 µm. Method: starting oven temp 35 °C, hold at 35 °C for 5 min, heat to 250 °C at 50 °C min^{-1}, hold at 250 °C for 5 min.

Synthesis

1) Preparation of complex 5

A solution of 2-(diphenylphosphino)-*N*-methylethanamine (0.51 g, 2.1 mmol) in toluene (10 mL) was added to a stirred solution of tris(triphenylphosphine)ruthenium(II) dichloride (1.00 g, 1.04 mmol) in toluene (30 mL). The mixture was stirred at 100 °C for 6 h, after which time the resulting suspension was allowed to cool and then filtered. The solid was washed with toluene (4 × 20 mL), until the filtrate was colourless, and dried under reduced pressure to give complex **5** (0.41 g, 60%) as an orange solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.28–6.99 (20H, m, Ar*H*), 4.03 (2H, br s, N*H*), 3.44-3.28 (2H, m, C*H*H), 2.79–2.74 (12H, m, CH*H*C*H*$_2$ and C*H*$_3$); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 60.2 (minor, s) 58.6 (major, s). ESI-MS: 658.07 [M$^+$], 623.11 [M$^+$ - Cl]. For spectra see Figures S1-S2.

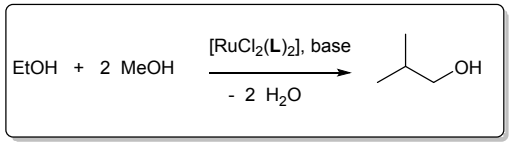
Catalysis

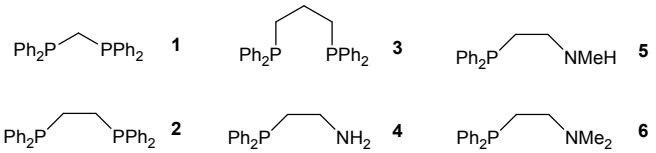
Catalytic reactions were carried out in a 100 mL Parr stainless steel autoclave with aluminium heating mantle and using magnetic stirring. A typical procedure is shown below. Full catalytic results are shown in Table S1.

1) Typical catalytic run

trans-[$RuCl_2$(dppm)]$_2$ (0.016 g, 0.017 mmol, 0.1 mol%) and sodium methoxide (1.85 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert. The insert was then sealed within the autoclave which was evacuated and re-filled with nitrogen 3 times. Methanol (10 mL) was injected into the autoclave through an inlet against a flow of nitrogen followed by ethanol (1 mL, 17.13 mmol). The autoclave was sealed and placed into the pre-heated (180 °C) aluminium heating mantle for 2 h. After the reaction run time, the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 µL of sample, 25 µL of *n*-pentanol standard, 1 mL MeOH).

Table S1. Ruthenium catalysed conversion of ethanol and methanol to isobutanol



L = 

Run[a]	Complex (mol%)[b]	Base (mol%)[b]	Temp/°C	Run Time/h	EtOH Conversion[c]	TON[d](Selectivity)[e][Yield]		
						Isobutanol	*n*-Propanol	Other
1	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (200)	180	2	66.4	651(98.1)[65.1]	12(1.8)[1.2]	1(0.1)[0.1]
2	[$RuCl_2$(**2**)$_2$] (0.1)	NaOMe (200)	180	2	3.3	31(95.4)[3.1]	2(4.6)[0.2]	-
3	[$RuCl_2$(**3**)$_2$] (0.1)	NaOMe (200)	180	2	4.7	28(59.2[2.8]	19(40.8)[1.9]	-
4	[$RuCl_2$(**4**)$_2$] (0.1)	NaOMe (200)	180	2	41.6	383(92.3)[38.3]	30(7.3)[3.0]	3(0.4)[0.3]
5	[$RuCl_2$(**4**)$_2$] (0.1)	NaOMe (200)	180	20	56.3	505(89.7)[50.5]	56(9.9)[5.6]	5(0.4)[0.5]
6	[$RuCl_2$(**5**)$_2$] (0.1)	NaOMe (200)	180	20	48.6	464(95.5)[46.4]	20(4.2)[2.0]	3(0.3)[0.3]
7	[$RuCl_2$(**6**)$_2$] (0.1)	NaOMe (200)	180	20	31.1	290(93.2)[29.0]	20(6.5)[2.0]	2(0.3)[0.2]
8	[$RuCl_2$(**1**)$_2$] (0.1)	NaO^{t}Bu (200)	180	2	55.2	541(98.0)[54.1]	10(1.9)[1.0]	1(0.1)[0.1]
9	[$RuCl_2$(**1**)$_2$] (0.1)	NaOH (200)	180	2	73.8	706(95.6)[70.6]	32(4.4)[3.2]	1(0.1)[0.1]
10	[$RuCl_2$(**1**)$_2$] (0.1)	KOH (200)	180	2	60.8	577(94.9)[57.7]	30(4.9)[3.0]	2(0.2)[0.2]
11	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (150)	180	2	69.6	679(97.5)[67.9]	24(2.5)[2.4]	-
12	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (100)	180	2	49.9	467(93.6)[46.7]	31(6.2)[3.1]	2(0.2)[0.2]
13	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (50)	180	2	12.0	108(90.2)[10.8]	11(8.9)[1.1]	2(0.8)[0.2]
14	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (200)	120	20	11.2	91(81.2)[9.1]	21(18.6)[2.1]	1(0.3)[0.1]
15	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (200)	150	20	67.1	644(96.0)[64.4]	26(3.9)[2.6]	1(0.1)[0.1]
16	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (200)	180	20	75.2	750(99.8)[75.0]	1(0.1)[0.1]	2(0.1)[0.2]
17	[$RuCl_2$(**1**)$_2$] (0.1)	NaOH (200)	180	2	66.7	640(96.0)[64.0]	26(3.9)[2.6]	1(0.1)[0.1]
18[f]	-	-	180	2	41.7	391(93.8)[39.1]	26(6.2)[2.6]	-
19	[$RuCl_2$(**1**)$_2$] (0.1)	NaOMe (200)	180	2	65.4	636(97.6)[63.6]	13(2.0)[1.3]	5(0.4)[0.5]
20[g]	[$RuCl_2$(**1**)$_2$] (0.05)	NaOMe (200)	180	2	51.7	508(98.2)[50.8]	9(1.8)[0.9]	-

21[h]	$[RuCl_2(\mathbf{1})_2]$ (0.03)	NaOMe (200)	180	2	42.5	417(98.0)[41.7]	8(2.0)[0.8]	-
22[i]	$[RuCl_2(\mathbf{1})_2]$ (0.1)	NaOH (200)	180	2	73.0	709(97.1)[70.9]	21(2.9)[2.1]	-

[a] Conditions: 1 mL ethanol, 10 mL methanol. [b] mol% based on ethanol substrate. [c] Total conversion of ethanol to liquid products, isobutanol, *n*-propanol and *n*-butanol. [d] TON based on mmol of substrate converted to products per mmol of Ru. [e] Total selectivity to products in the liquid fraction determined by GC. [f] Solid product from run 17 used as catalyst/base, fresh ethanol (1 mL) and methanol (10 mL) added. [g] A solution of NaOMe (34.26 mmol) in ethanol/methanol (1/10 mL) was added to the product mixture from run 19, [Ru] = 0.05 mol% based on ethanol. [h] A solution of NaOMe (34.26 mmol) in ethanol/methanol (1/10 mL) was added to the product mixture from run 20, [Ru] = 0.03 mol% based on ethanol. [i] 0.62 mL water added.

2) Water inhibition experiment

trans-[$RuCl_2$(dppm)]$_2$ (0.016 g, 0.017 mmol, 0.1 mol%) and powdered sodium hydroxide (1.37 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert. The insert was then sealed within the autoclave which was evacuated and re-filled with nitrogen 3 times. Methanol (10 mL) was injected into the autoclave through an inlet against a flow of nitrogen followed by ethanol (1 mL, 17.13 mmol) and degassed water (0.62 mL, 34.41 mmol, 201 mol%). The autoclave was sealed and placed into the pre-heated (180 °C) aluminium heating mantle for 2 h. After the reaction run time, the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 µL of sample, 25 µL of *n*-pentanol standard, 1 mL MeOH). Results are shown in Table S1.

3) Recycling experiments

3.1. Addition of fresh substrate

trans-[$RuCl_2$(dppm)]$_2$ (0.016 g, 0.017 mmol, 0.1 mol%), and powdered sodium hydroxide (1.37 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert. The insert was then sealed within the autoclave which was then evacuated and re-filled with nitrogen 3 times. Methanol (10 mL) was injected into the autoclave through an inlet against a flow of nitrogen followed by ethanol (1 mL, 17.13 mmol). The autoclave was sealed and placed into the pre-heated (180 °C) aluminium heating mantle for 2 h. After the reaction run time, the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction through a N_2/vacuum manifold to ensure the autoclave contents were kept under an inert atmosphere. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 µL of sample, 25 µL of *n*-pentanol standard, 1 mL MeOH). Liquid products were removed from the autoclave by vacuum transfer for 6 h at 60 °C. The autoclave was transfered to a glove box and opened. The white solid residue was scraped off the sleeve walls and ground into a fine powder. This powder was placed back into the PTFE insert, sealed within the autoclave and transferred to the N_2/vacuum manifold. Fresh methanol (10 mL) and ethanol (1 mL) were added and the catalysis was repeated as above. Results are shown in Table S1.

3.2. Addition of fresh base and substrate

trans-[$RuCl_2$(dppm)]$_2$ (0.016 g, 0.017 mmol, 0.1 mol%), and sodium methoxide (1.85 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert. The insert was then sealed within the autoclave which was then evacuated and re-filled with nitrogen 3 times. Methanol (10 mL) was injected into the autoclave through an inlet against a flow of nitrogen followed by ethanol (1 mL, 17.13 mmol). The autoclave was sealed and placed into the pre-heated (180 °C) aluminium heating mantle for 2 h. After the reaction run time, the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction through a N_2/vacuum manifold to ensure the autoclave contents were kept under an inert atmosphere. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 µL of sample, 25 µL of *n*-pentanol standard, 1 mL MeOH). A solution of sodium methoxide (1.85 g, 34.26 mmol) dissolved in ethanol/methanol (1/10 mL) was injected into the autoclave through an inlet against a flow of nitrogen and the catalysis was repeated as above. After 2 hours the autoclave was allowed to cool and vented through a N_2/vacuum manifold. A liquid sample was removed for GC analysis. A solution of sodium methoxide (1.85 g, 34.26 mmol) dissolved in ethanol/methanol (1/10 mL) was injected into the autoclave through an inlet against a flow of nitrogen and the catalysis was

repeated once more as above. Results are shown in Table S1. A bar chart showing mmol of isobutanol formed during each cycle is shown in Figure S1.

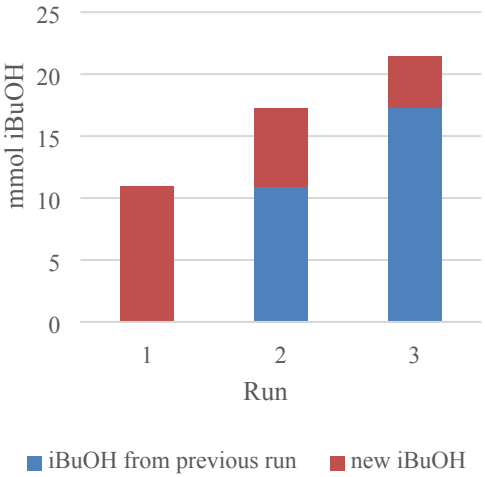


Figure S1. Bar chart showing mmol of isobutanol present in the autoclave after each cycle.

2) Labelling study

trans-[$RuCl_2$(dppm)]$_2$ (0.016 g, 0.017 mmol, 0.1 mol%), and sodium methoxide (1.85 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert. The insert was then sealed within the autoclave which was then evacuated and re-filled with nitrogen 3 times. Methanol (9.5 mL) was injected into the autoclave through an inlet against a flow of nitrogen followed by ^{13}C labelled methanol (0.5 mL) and ethanol (1 mL, 17.13 mmol). The autoclave was sealed and placed into the pre-heated (180 °C) aluminium heating mantle for 2 h. After the reaction run time, the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction. A liquid sample was removed (0.7 mL) and analysed by $^{13}C\{^1H\}$ NMR spectroscopy. The spectrum was compared to that obtained from a standard run (see Figures S4 and S5). GC analysis indicated isobutanol was produced in a yield of 65.1% (98.3% selectivity in the liquid fraction).

Spectra

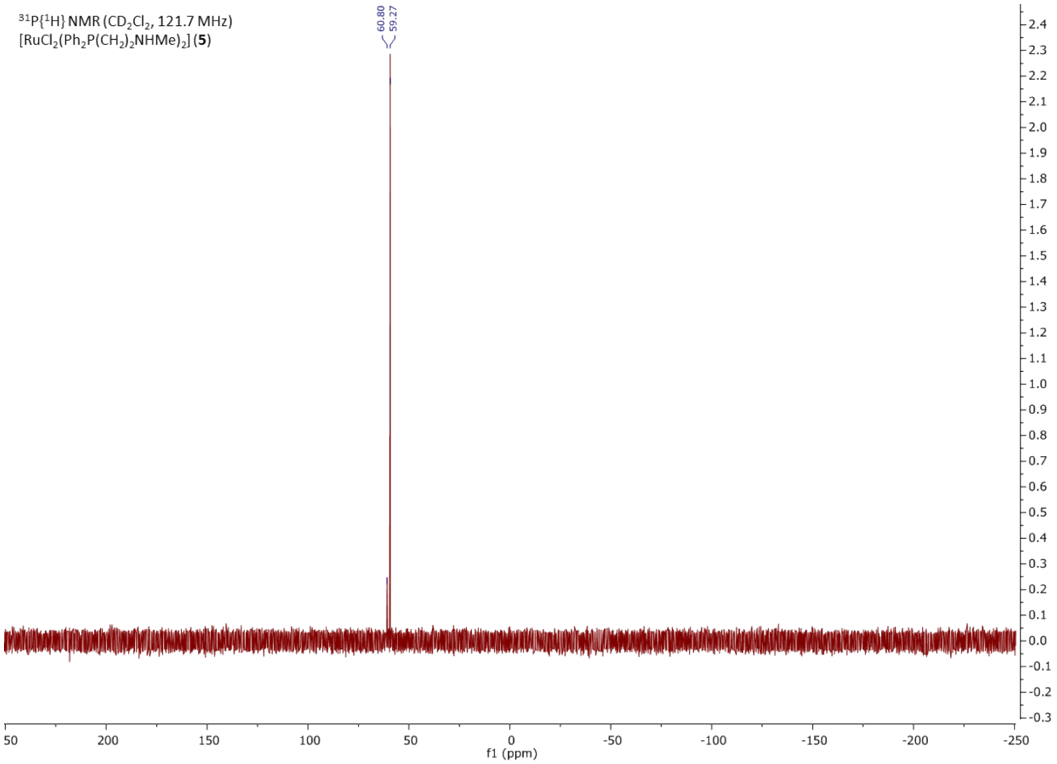


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of $[RuCl_2(Ph_2P(CH_2)_2NHMe)_2]$, **5** in CD_2Cl_2

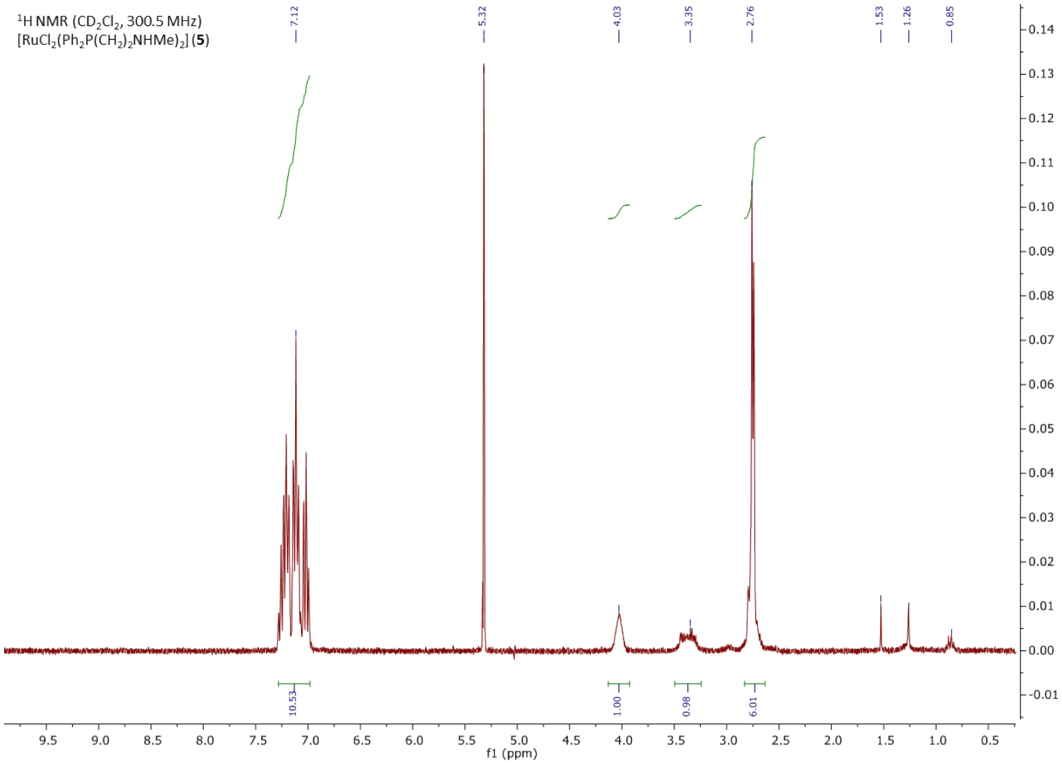


Figure S3. ^{1}H NMR spectrum of $[RuCl_2(Ph_2P(CH_2)_2NHMe)_2]$, **5** in CD_2Cl_2

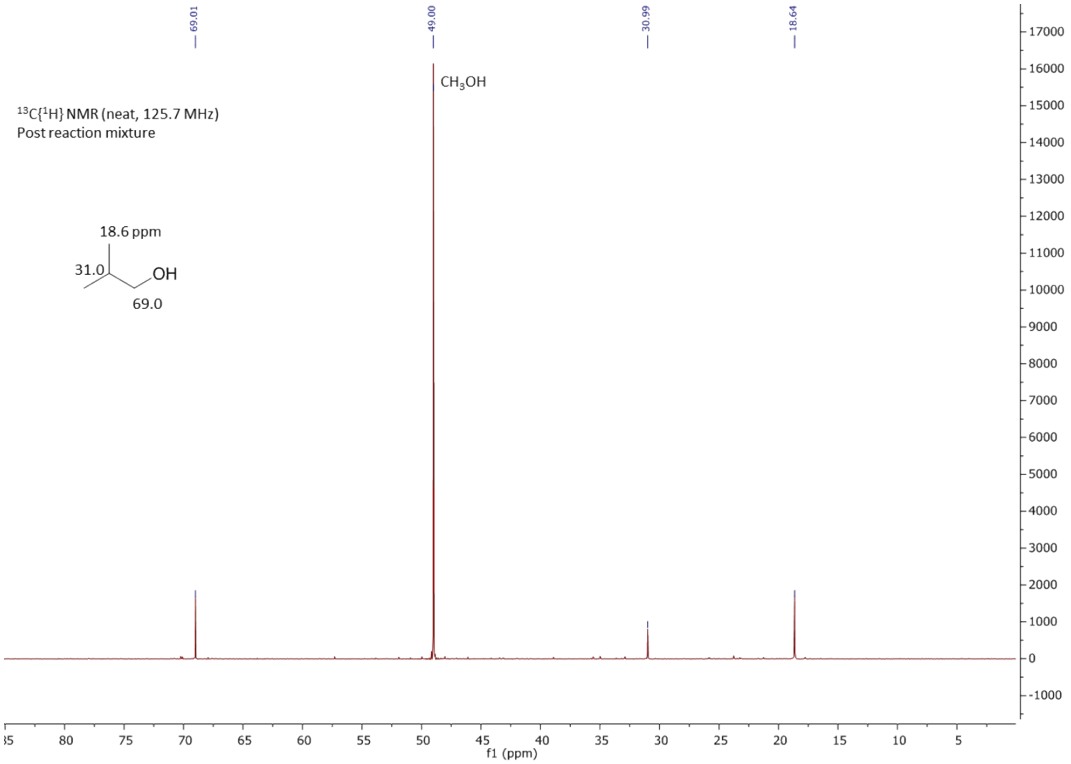


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of post catalysis mixture of a standard run (10 mL CH_3OH, 1 mL EtOH, 200 mol% NaOMe, 0.1 mol% $[RuCl_2(dppm)_2]$ (**1**), 180 °C, 2h)

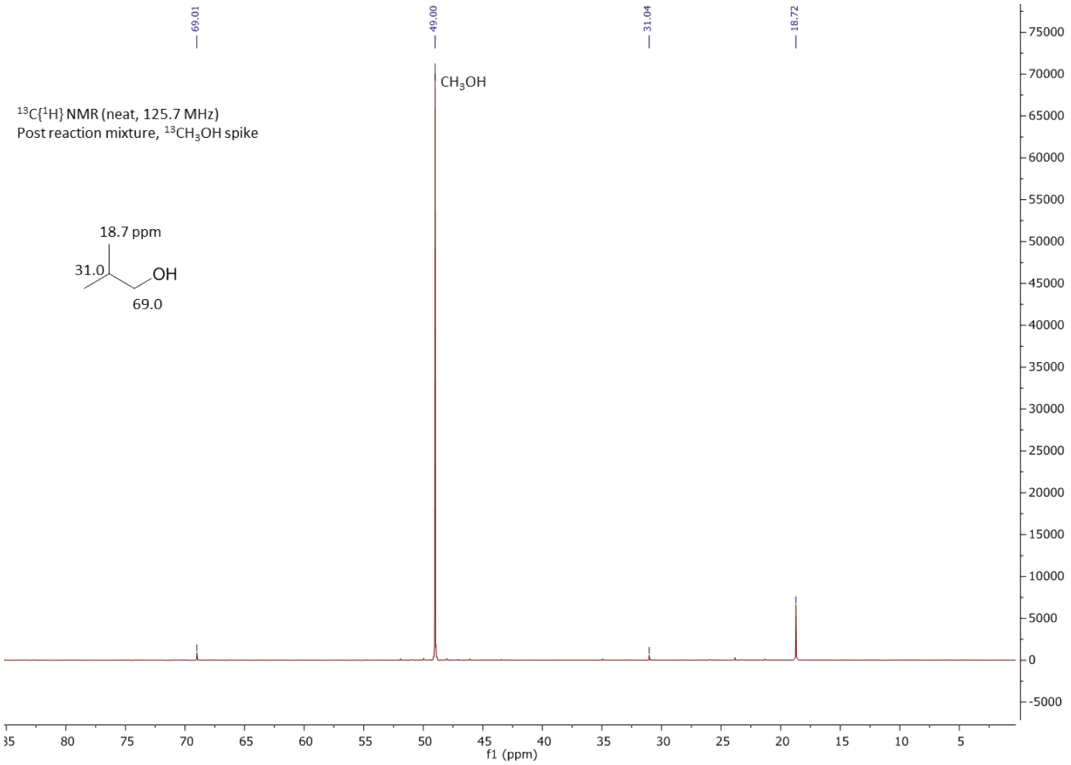


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of post catalysis mixture of run spiked with ^{13}C labelled methanol (9.5 mL MeOH, 0.5 mL $^{13}CH_3OH$, 1 mL EtOH, 200 mol% NaOMe, 0.1 mol% $[RuCl_2(dppm)_2]$ (**1**), 180 °C, 2h)

References

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